

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

20 JUL 1999 015751  
**PCT**

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**30 pages**

NOTIFICATION OF TRANSMITTAL OF  
INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing  
(day/month/year)

**20.07.99**

Applicant's or agent's file reference

**JHC/P40458WO**

**IMPORTANT NOTIFICATION**

International application No.

**PCT/US 98/04513**

International filing date (day/month/year)

**06/03/1998**

Priority date (day/month/year)

**07/03/1997**

Applicant

**WILLIAM MARSH RICE UNIVERSITY et al.**

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

**4. REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

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## PATENT C OPERATION TREATY


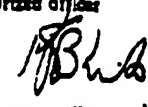
## PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>JHC/P40458WO</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/US 98/ 04513</b>	International filing date (day/month/year) <b>06/03/1998</b>	Priority date (day/month/year) <b>07/03/1997</b>
International Patent Classification (IPC) or national classification and IPC <b>C01B31/02</b>		
Applicant <b>WILLIAM MARSH RICE UNIVERSITY et al.</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 12 sheets, including this cover sheet.
- ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  
These annexes consists of a total of 17 sheets.
3. This report contains indications relating to the following items:
- I ☒ Basis of the report
  - II ☐ Priority
  - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV ☒ Lack of unity of invention
  - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI ☒ Certain documents cited
  - VII ☐ Certain defects in the international application
  - VIII ☐ Certain observations on the international application

Date of submission of the demand <b>05/10/1998</b>	Date of completion of this report <b>20.07.99</b>
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523856 epmu d Fax: (+49-89) 2399-4465	Authorized officer  <b>iv. E. Arn ttz</b> <b>P.P.</b> Telephone No. <b>Peter Lesniak</b>

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## I. Basis of the report

1. This report has been drawn up on the basis of (Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)

☐ the international application as originally filed

☒ the description, pages 1-81

pages

pages

, as originally filed

, filed with the demand

, filed with the letter of

☒ the claims, Nos.

Nos.

Nos.

Nos.

1-182

, as originally filed

, as amended under Article 18

, filed with the demand

, filed with the letter of

14.5.1999

☒ the drawings, sheets / fig. 1/21-21/21

sheets / fig.

sheets / fig.

, as originally filed

, filed with the demand

, filed with the letter of

2. The amendments have resulted in the cancellation of:

☐ the description, pages:

☐ the claims, Nos.

☐ the drawings, sheets / fig.

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2 (c)).

4. Additional observations, if necessary:

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## IV. Lack of unity of invention

1. In response to the invitation (Form PCT/PEA/408) to restrict or pay additional fees the applicant has:

- ☐ restricted the claims.
- ☒ paid additional fees.
- ☐ paid additional fees under protest.
- ☐ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is:

- ☐ complied with.
- ☐ not complied with for the following reasons:

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

- ☒ all parts.
- ☐ the parts relating to claims Nos.

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## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

## 1. Statement

Novelty	Claims	1-17, 18-105, 107, 111-116, 117-162	YES
	Claims	106, 108	NO
Inventive Step	Claims	1-17, 24-30, 31-62, 81-105, 111-116, 141-156	YES
	Claims	18-23, 63-71, 72-80, 107, 109-110, 117-140, 157-162	NO
Industrial Applicability	Claims	1-162	YES
	Claims		NO

## 2. Citations and Explanations

The following documents (D) are referred to in this communication; the numbering will be adhered to in the rest of the procedure:

- D<sub>1</sub> = Chemical Abstracts vol. 125 No. 16, 14 October 1996,  
AN 125:210949, XP002070313
- D<sub>2</sub> = Advanced Materials vol. 7 No. 3 March 1995, pp 275-276,  
Hlura et al
- D<sub>3</sub> = Electrochemical Society Proceedings vol. 95.110,  
Guo et al. pages 636-647
- D<sub>4</sub> = Science of Fullerenes and Carbon Nanotubes  
M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, 1995  
pages 765 and following.
- D<sub>5</sub> = WO96/18059
- D<sub>6</sub> = EP-A-591 595
- D<sub>7</sub> = WO96/38705
- D<sub>8</sub> = Chemical physics letters 260 (1996) 471-475  
"Single-wall nanotubes produced by metal-catalyzed  
disproportionation of carbon monoxide"
- D<sub>9</sub> = Applied physics letters 71 (18) 3 November 1997  
"Length control of individual carbon nanotubes by  
nanostructuring with a scanning tunnelling microscope".

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VI. Certain documents cited

1. Certain published documents (Rule 70.10)

Application no. Patent No.	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
WO 98/05920	12.02.98	08.08.97	08.08.96
US 5698175	16.12.97	03.07.95	05.07.94
WO 97/09275	13.03.97	06.08.96	08.09.95
			08.05.96
			26.07.96

2. Non-written disclosures (Rule 70.9)

Kind of non-written disclosure	Date of non-written disclosure (day/month/year)	Date of written disclosure referring to non-written disclosure (day/month/year)
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Group AClaims 1-17

1. The main argument of the applicant is that what is established for MWNT is not necessarily valid for SWNT. This is certainly correct but would remain a purely theoretical argument if no further elements of comparison were given. The applicant states that single wall nanotubes are fundamentally different from multi-wall nanotubes. The single wall tubes are individual molecules, whereas the multiwall tubes are basically a cylindrical form of graphite. The single-wall tubes have remarkable mechanical, electrical and thermal characteristics because they are essentially perfect *molecules*. The multi-wall tubes are characterized by a much higher density of crystalline defects, which changes their physical properties in fundamental ways.
2. The argument under 1 hereinbefore can be accepted.
3. It is unclear whether D<sub>1</sub> relates to MWNT or to SWNT. Nevertheless, the applicant must get the benefit of the doubt. As far as D<sub>2</sub> is concerned, it can be reasonably accepted that it probably relates to MWNT (see p 275 left column lines 3-4 and p 276 left column, last §).

Therefore, the applicant's argumentation towards claims 1-17 is accepted and claims 1-17 regarded as being novel and inventive over the available prior art documents.

Claims 63-71

(a) The arguments of the applicant are rejected since

- (1) it is not correct to state that claims 63-66 are directed to "purified SWNT" (see page 2 of the applicant's letter). They merely refer to "a composition of matter" which could for instance be in an as-synthesized state.
- (2) Neither does said claims indicate whether said "composition of matter" is macroscopic or microscopic.

Therefore, the original objection (4-8) is maintained:

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- (b) The term "composition of matter" is unclear. Here, it is interpreted as meaning "a carbonaceous material".
- (c) The wording of claim 63 is extremely broad, so that it is felt that any bundle of SWNT anticipates claim 63. Such bundles are for instance to be seen on page 646 of D<sub>3</sub>, but also on page 767 of D<sub>4</sub> (see comment on page 765 2nd paragraph).

The same arguments are brought forward vis-à-vis of claims 64-66, 67-71.

Therefore claims 63-71 are regarded as lacking an inventive step.

Claims 72-80

- Claim 72 is unclear since it now states that  $n$  is from "0 to 30" but at the same time requires that "the tubular carbon molecules contains at least one of R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, therefore necessitating  $n$  to be  $>0$ .

It is suggested to limit  $n$  to values 1-30.

The following comments are made supposing this suggestion is followed

According to the applicant, D<sub>6</sub> does not relate to SWNT (see page 7, lines 33-35 of D<sub>5</sub>) functionalized in a variety of ways.

- Nevertheless, the SWNT of D<sub>4</sub> (see pages 758; 770, 2nd paragraph and Fig. 19.10(c) on page 772) can readily be derivatized, i.e. functionalized by following the teaching of D<sub>6</sub> (see for instance D<sub>6</sub>'s general statement on page 1 lines 1-14).
- D<sub>4</sub> also discloses filled nanotubes (see page 858).
- Since none of claims 72-80 contain any quantitative information on the degree of derivatization, it is considered that they lack an inventive step over D<sub>4</sub> combined with D<sub>6</sub>.



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Claims 106-110

Endohedrally-loaded tubular carbon molecules are known for instance from

D<sub>4</sub> (see 3.d herein above).

D<sub>4</sub> also discloses (see chapter 20) many possible applications.

D<sub>5</sub> teaches that endohedrally doped fullerenes can be used as memory bit.  
(Compare with present application, page 51, lines 4-8).

the endohedrally loaded nanotubes of D<sub>4</sub> can be for instance loaded with "compounds of Gd, Yt, Mn", (see page 859, 2nd paragraph).

Since the wording of claim 106 does not specify any kind of endohedral species<sup>S</sup> it is considered that it is anticipated by D<sub>4</sub>.

The same conclusion is valid for claim 108.

D<sub>4</sub> does not explicitly recite or support C<sub>60</sub> or C<sub>70</sub> a possible endohedral species (as in present claim 107), but it is considered to be within the reach of the skilled practitioner knowing D<sub>4</sub> and D<sub>5</sub> to extend said teaching so as to obtain a SWNT with C<sub>60</sub> or C<sub>70</sub> as endohedral species.

Consequently claim 107 is regarded as lacking an inventive step.

The same conclusion is made for claims 109-110.

Claims 117-140

D<sub>5</sub> discloses on page 12 lines 8-17 carbon fibrils, ie nanotubes (see page 11 lines 7-30) which can be "incorporated in a matrix"; - the matrix preferably being an organic polymer, eg a thermoset resin such as epoxy, bismaleimide, polyamide; a thermoplastic resin; a metal or a ceramic material.

According to the applicant, D<sub>5</sub> merely relates to MWNT.

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It has been noted that the applicant's argumentation relates to the fact that processes which are valid for MWNT are not necessarily effective for SWNT. Nevertheless this argument can not be successful here because claim 117 does not recite any technical characteristic of the composite material, so that what should have been demonstrated is that by using the technic of D<sub>5</sub> with SWNT, no composite at all can be obtained.

Nevertheless, the examiner opines that this is very unlikely to be the case, so that claim 117 is regarded as lacking in inventive step.

The same conclusion applies to claims 118-124, 131.

Claims 125-130 and 132-140 are regarded as lacking an inventive step since it cannot be seen what technical problem a man skilled in the art knowing D<sub>5</sub> would have had to solve inventively to come to the preferred embodiments of claims 125-130.

Claims 141-152

An objection was raised on the base of D<sub>5</sub>.

Nevertheless, the applicant considers that D<sub>5</sub> deals with multiwall nanotubes laden with crystal defects, which is not predictive of the behaviour of the SWNT in claims 141-152.

The argument is here accepted.

Therefore claims 141-152 are regarded as being novel and inventive over the available prior art.

Claims 153-156

As far as claims 153-156 are concerned, it appears that none of the available prior art literature suggest or discloses an antenna such as that claimed by present claim 153.

D<sub>4</sub>, chapter 20, teaches that a polymeric -C<sub>60</sub> heterojunction is expected to exhibit a photovoltaic response (page 881). D<sub>4</sub> also gives on figure 20.2 (page 903) a schematic presentation of several proposed electronic device applications for carbon nanotubes.

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Nevertheless, no-explicit mention that a current could be generated through photo conductivity of such a tube is suggested or disclosed.

Therefore, claims 153-156 are both novel and inventive.

Claims 157-162

Considering D<sub>4</sub> page 903 fig. 20.2 as well as page 904 and D<sub>7</sub>, for instance claims 36, 41, 45, 50, 53-55 etc... It cannot be seen what technical problem the skilled practitioner had to solve - in an inventive manner - to come to the embodiments of present claims 157-162.

Therefore these are considered as not being inventive.

Group B: Claims 18-30Claim 18

It is not clear whether by "said molecules having substantially equal lengths" is meant that these molecules merely should have any length within the range 5-500 nm or whether an average length within said range is meant.

D<sub>6</sub> discloses on page 473 right column first two lines, SWNT having a length ranging from 100 nm up to several microns.

At least one cutting technique is known from D<sub>6</sub>.

Process step c) merely refers to an isolation procedure which is not precisely disclosed. Therefore, the isolation - purification procedures known in the art (see D<sub>1</sub>, D<sub>2</sub>, D<sub>4</sub> ..... ) are encompassed by said process step, which therefore cannot be regarded as being inventive.

Therefore, claim 18 is felt to lack an inventive step.

- Claims 19-23 relate to a preferred cutting method comprising using a "high energy beam of high mass ions".
- D<sub>6</sub> describes a cutting method comprising injecting electrons into the nanotubes at 'a

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relatively high voltage" (page 2631 right column, paragraph before last).

- Therefore claims 19-23 are novel over the available prior art literature.
- Nevertheless it cannot be seen to what specific advantage, or to what unexpected effect, the use of high mass ions instead of electrons leads to. Why would the skilled practitioner knowing  $D_0$  not be inclined to try cutting nanotubes with projectiles other than electrons?

Therefore it is considered that the use of a "high energy beam of high mass ions" is a technically equivalent mean for cutting nanotubes.

Therefore, claims 19-23 lack an inventive step.

- Claims 24-25 relate to another cutting method, comprising sonicating with acoustic energy a suspension of SWNT in a medium.

Since none of the documents cited in the search report mention or suggest that nanotubes could be cut by using sonication (as described on page 26 lines 23 - page 27 line 19) present claims 24-25 are regarded as being novel and inventive.

- None of the available prior art documents suggest that SWNT can be cut by refluxing the same in concentrated  $HNO_3$ .

Therefore claims 26-30 are considered as being inventive.

Group C: Claims 31-62, 81-105, 111-116

- $D_5$  appears to be the most relevant prior art document.
- None of the documents of the I.S.R. disclose or suggest methods for forming a macroscopic molecular array of tubular carbon molecules
- Therefore present claims 31-62 must be considered as novel and inventive over said documents.

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- Moreover, the macroscopic molecular array of independent claim 81 as well as the product of claim 91 are neither disclosed nor suggested by the available prior art literature.
- Therefore, claims 81-105 are both novel and inventive; the same conclusion applies to claims 111-116.

We Claim:

1. A method for purifying a mixture comprising single-wall carbon nanotubes and amorphous carbon contaminate, said method comprising the steps  
5 of:
  - (a) heating said mixture under oxidizing conditions sufficient to remove the said amorphous carbon and
  - (b) recovering a product comprising at least about 80% by weight of single-wall carbon nanotubes.
- 10 2. The method of claim 1 wherein said oxidizing conditions comprise an aqueous solution of an inorganic oxidant.
3. The method of claim 2 wherein said inorganic oxidant is selected from the group consisting of nitric acid, a mixture of sulfuric acid and hydrogen peroxide, potassium permanganate and mixtures thereof.
- 15 4. The method of claim 2 wherein said aqueous solution is heated to reflux.
5. The method of claim 2 additionally comprising the step of subjecting the oxidized product of step (b) to a saponification treatment.
6. The method of claim 5 wherein said saponification treatment  
20 comprises contacting said product with a basic solution.
7. The method of a claim 6 wherein said basic solution comprises sodium hydroxide.
8. The method of claim 6 additionally comprising the step of neutralizing the saponified product with an acid.
- 25 9. The method of claim 8 wherein said acid is hydrochloric acid.
10. The method of claim 8 additionally comprising the step of recovering a solid product from the saponified, neutralized product.
11. The method of claim 10 wherein said product is recovered by a method selected from the group consisting of filtration, settling by gravity,  
30 chemical flocculators, and liquid cycloning.

- 12 The method of claim 10 wherein said solid product is a paper-like two dimensional product.
13. The method of claim 12 additionally comprising the step of drying the product.
- 5 14. The method of claim 13 wherein said product is dried at about 850°C in a hydrogen gas atmosphere.
15. The method of claim 1 wherein said product comprises at least about 90% by weight of single-wall carbon nanotubes.
16. The method of claim 1 wherein said product comprises at least  
10 about 95% by weight of single-wall carbon nanotubes.
17. The method of claim 1 wherein said product comprises at least about 99% by weight of single-wall carbon nanotubes.
18. A method for producing tubular carbon molecules of about 5 to 500 nm in length, said method comprising the steps of:
- 15 (a) providing a single-wall carbon nanotube-containing material;
- (b) cutting single-wall nanotubes in said single-wall nanotube containing-material to form a mixture of tubular carbon molecules having lengths in the range of 5-500 nm;
- (c) isolating from said mixture of tubular carbon molecules a fraction  
20 of said molecules having substantially equal lengths.
19. The method of claim 18 wherein said cutting single-wall nanotubes into tubular carbon molecules comprising the steps of:
- (a) forming a substantially two-dimensional target containing single-wall nanotubes of lengths up to about one micron or more, and
- 25 (b) irradiating said target with a high energy beam of high mass ions.
20. The method of claim 19 wherein a high energy beam is produced in a cyclotron and has an energy of from about 0.1 to about 10 GeV.
21. The method of claim 19 wherein said high mass ion has a mass of greater than about 150 AMU.

22. The method of claim 21 wherein said high mass ion is selected from the group consisting of gold, bismuth and uranium.

23. The method of claim of 22 wherein the high mass ion is  $Au^{+3}$

5 24. The method of claim 18 wherein said cutting single-wall nanotubes into tubular carbon molecules comprises the steps of:

(a) forming a suspension of single-wall nanotubes in a medium;

(b) sonicating said suspension with acoustic energy.

10 25. The method of claim 24 wherein said acoustic energy is produced by a device operating at 40 KHz and having an output of 20 W.

26. The method of claim 18 wherein said cutting single-wall nanotubes into tubular carbon molecules comprises refluxing single wall carbon nanotube containing material in concentrated  $HNO_3$ .

15 27. The method of claim 19 further comprising the step of heating the tubular carbon molecules to form a hemispheric fullerene cap on at least one end thereof.

28. The method of claim 18 further comprising the step of reacting said tubular carbon molecules with a material which provides at the reaction conditions at least one substituent on at least one of said ends of said tubular carbon molecule.

20 29. The method of claim 26 further comprising the step of reacting said tubular carbon molecules with a material which provides at the reaction conditions at least one substituent on at least one of said ends of said tubular carbon molecule.

25 30. The method of claim 28 or 29 wherein said substituent is selected from the group consisting of each may be independently selected from the group consisting of hydrogen; alkyl, acyl, aryl, aralkyl, halogen; substituted or unsubstituted thiol; unsubstituted or substituted amino; hydroxy, and  $OR'$  wherein  $R'$  is selected from the group consisting of hydrogen, alkyl, acyl, aryl, aralkyl, unsubstituted or substituted amino; substituted or unsubstituted thiol; and halogen; and a linear or cyclic carbon chain optionally interrupted with one or more



heteroatom, and optionally substituted with one or more =O, or =S, hydroxy, an aminoalkyl group, an amino acid, or a peptide of 2-8 amino acids.

31. A method for forming a macroscopic molecular array of tubular carbon molecules, said method comprising the steps of:

- 5 (a) providing at least about  $10^6$  tubular carbon molecules of substantially similar length in the range of 50 to 500 nm;
- (b) introducing a linking moiety onto at least one end of said tubular carbon molecules;
- (c) providing a substrate coated with a material to which said linking moiety will attach; and
- 10 (d) contacting said tubular carbon molecules containing a linking moiety with said substrate.

32. The method of claim 31 wherein said substrate is selected from the group consisting of gold, mercury and indium-tin-oxide.

15 33. The method of claim 32 wherein said linking moiety is selected from the group consisting of -S-,  $-S-(CH_2)_n-NH-$ , and  $-SiO_3(CH_2)_nNH_2$ .

34. A method for forming a macroscopic molecular array of tubular carbon molecules, said method comprising the steps of:

- (a) providing a nanoscale array of microwells on a substrate;
- 20 (b) depositing a metal catalyst in each of said microwells; and
- (c) directing a stream of hydrocarbon or CO feedstock gas at said substrate under conditions that effect growth of single-wall carbon nanotubes from each microwell.

35. The method of claim 34 further comprising the step of applying an electric field in the vicinity of said substrate to assist in the alignment of said nanotubes growing from said microwells.

36. A method for forming a macroscopic molecular array of tubular carbon molecules, said method comprising the steps of:

- (a) providing surface containing purified but entangled and relatively
- 30 endless single-wall carbon nanotube material;

(b) subjecting said surface to oxidizing conditions sufficient to cause short lengths of broken nanotubes to protrude up from said surface; and

(c) applying an electric field to said surface to cause said nanotubes protruding from said surface to align in an orientation generally perpendicular to said surface and coalesce into an array by van der Waals interaction forces.

37. The method of claim 36 wherein said oxidizing conditions comprise heating said surface to about 500°C in an atmosphere of oxygen and CO<sub>2</sub>.

38. A method of forming a macroscopic molecular array of tubular carbon molecules, said method comprising the step of assembling subarrays of up to 10<sup>6</sup> single-wall carbon nanotubes into a composite array.

39. The method of claim 38 wherein all the subarrays have the same type of nanotubes.

40. The method of claim 38 wherein the subarrays have different types of nanotubes.

41. The method of claim 38 wherein the subarrays are made according to the method of any of claims 31, 34 or 36.

42. A method for continuously growing macroscopic carbon fiber comprising at least about 10<sup>6</sup> single-wall nanotubes in generally parallel orientation, said method comprising the steps of:

(a) providing a macroscopic molecular array of at least about 10<sup>6</sup> tubular carbon molecules in generally parallel orientation and having substantially similar lengths in the range of from about 50 to about 500 nanometers;

(b) removing the hemispherical fullerene cap from the upper ends of the tubular carbon molecules in said array;

(c) contacting said upper ends of the tubular carbon molecules in said array with at least one catalytic metal;

- (d) supplying a gaseous source of carbon to the end of said array while applying localized energy to the end of said array to heat said end to a temperature in the range of about 500° C to about 1300° C; and
- (e) continuously recovering the growing carbon fiber.

5 43. The method of claim 42 wherein said fullerene caps are removed by heating in an oxidative environment.

44. The method of claim 43 wherein said oxidative environment comprises aqueous etching with nitric acid or gas phase etching at temperatures of about 500° C in an atmosphere of oxygen and CO<sub>2</sub>.

10 45. The method of claim 42 wherein said catalytic metal is selected from the group consisting of Group VIII transition metals, Group VI transition metals, metals of the lanthanide series, metals of the actinide series, and mixtures thereof.

15 46. The method of claim 45 wherein said catalytic metal is selected from the group consisting of Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt.

47. The method of claim 46 wherein said catalytic metal is selected from the group consisting of Fe, Ni, and Co, and mixtures thereof.

48. The method of claim 45 wherein said catalytic metal is selected from the group consisting of Cr, Mo, and W.

20 49. The method of claim 42 wherein said catalytic metal is deposited in situ on each nanotube as a metal atom cluster.

50. The method of claim 49 wherein said metal atom cluster has from about 10 to about 200 metal atoms.

25 51. The method of claim 42 wherein said catalytic metal is deposited as preformed nanoparticles.

52. The method of claim 51 wherein said catalytic metal is Mo.

53. The method of claim 42 wherein said catalytic metal is deposited in the form of a metal precursor selected from the group consisting of salts, oxides and complexes of said metal.

54. The method of claim 42 wherein said catalytic metal is deposited by evaporating metal atoms and allowing them to condense and coalesce on said open nanotube ends.

55. The method of claim 54 wherein said evaporation is effected by heating a wire or wires containing said catalytic metal.

56. The method of claim 54 wherein said evaporation is effected by molecular beam evaporation.

57. The method of claim 42 wherein gaseous source of carbon is selected from the group consisting of hydrocarbons and carbon monoxide.

58. The method of claim 57 wherein said hydrocarbon is selected from the group consisting of alkyls, acyls, aryls and aralkyl having 1 to 7 carbon atoms.

59. The method of claim 58 wherein said hydrocarbon is methane, ethane, ethylene, acetylene, acetone, propane, propylene and mixtures thereof.

60. The method of claim 42 wherein said localized energy is provided by a laser beam.

61. The method of claim 42 wherein said localized energy is provided by a source selected from the group consisting of a microwave generator, an R-F coil and a solar concentrator.

62. The method of claim 42 wherein said end is heated to a temperature in the range of about 900°C to about 1100°C.

63. A composition of matter comprising at least about 80% by weight of single-wall carbon nanotubes.

64. The composition of claim 63 comprising at least about 90% by weight of single-wall carbon nanotubes.

65. The composition of claim 63 comprising at least about 95% by weight of single-wall carbon nanotubes.

66. The composition of claim 63 comprising at least about 99% by weight of single-wall carbon molecules.

67. A felt comprising at least about 80% by weight of single-wall carbon nanotubes.

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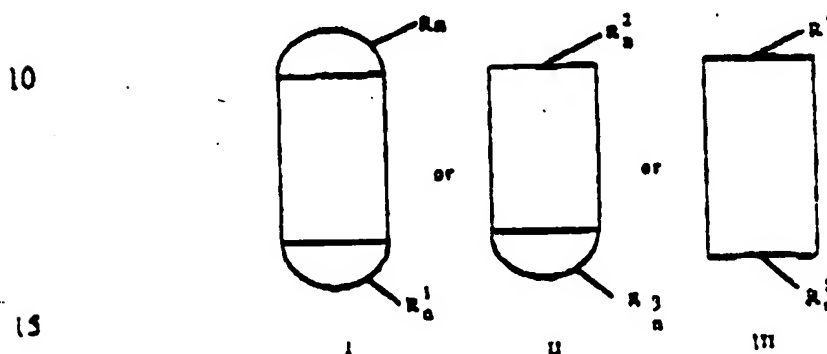
68. The felt of claim 67 comprising at least about 90% by weight of single-wall nanotubes.

69. The felt of claim 67 comprising at least about 95% by weight of single-wall nanotubes.

70. The felt of claim 67 comprising at least about 99% by weight of single-wall nanotubes.

71. The felt of claim 67 in the form of a paper-like material.

72. A tubular carbon molecule having the following structure:



where

20



is a substantially defect-free cylindrical graphene sheet (optionally doped with noncarbon atoms) having from about  $10^2$  to  $10^6$  carbon atoms;

25

where



is a hemispherical fullerene cap having at least six pentagons and the remainder hexagons;

30

n

is a number from 0 to 30; and

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R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup>

each may be independently selected from the group consisting of hydrogen; alkyl; acyl; aryl; aralkyl; halogen; substituted or unsubstituted thiol; unsubstituted or substituted amino; hydroxy, and OR' wherein R' is selected from the group consisting of hydrogen, alkyl, acyl, aryl, aralkyl, unsubstituted or substituted amino; substituted or unsubstituted thiol; and halogen; and a linear or cyclic carbon chain optionally interrupted with one or more heteroatom, and optionally substituted with one or more =O, or =S, hydroxy, an aminoalkyl group, an amino acid, or a peptide of 2-8 amino acids, wherein the tubular carbon molecule contains at least one of R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, or R<sup>5</sup>.

73. The molecule of claim 72 wherein said graphene sheet has a configuration that corresponds to a (n,n) single-wall carbon nanotube

74. The molecule of claim 72 wherein said molecule has a length from about 5 to about 1000 nm.

75. The molecule of claim 74 wherein said molecule has a length of from about 5 to about 500 nm.

76. The molecule of claim 72 wherein n is 0 to 12.

77. The molecule of claim 72 further comprising at least one endohedral species.

78. The molecule of claim 77 wherein said endohedral species is selected from the group consisting of metal atoms, fullerene molecules, other small molecules and mixture thereof.

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79. The molecule of claim 78 comprising a (10,10) single-wall nanotube containing at least one endohedral species selected from the group consisting of  $C_{60}$ ,  $C_{70}$  or mixtures thereof.

80. The molecule of claim 79 wherein said  $C_{60}$  or  $C_{70}$  additionally contains an endohedral substituent selected from the group consisting of metal atoms and metal compounds.

81. A macroscopic molecular array comprising at least about  $10^6$  single-wall carbon nanotubes in generally parallel orientation and having substantially similar lengths in the range of from about 5 to about 500 nanometers.

82. The array of claim 81 wherein said nanotubes are of the same type.

83. The array of claim 82 wherein said nanotubes are of the (n,n) type.

84. The array of claim 83 wherein said nanotubes are of the (10,10) type.

85. The array of claim 83 wherein said nanotubes are of the (m,n) type.

86. The array of claim 81 wherein said nanotubes are of different types.

87. The array of claim 81 further comprising a substrate attached to one end of said array and oriented substantially perpendicularly to the nanotubes in said array.

88. The array of claim 87 wherein said substrate is a bucky paper surface.

89. The array of claim 87 wherein said substrate is a metal layer selected from the group consisting of gold, mercury and indium-tin-oxide.

90. The array of claim 86 wherein a central portion of nanotubes are of the (n,n) type and an outer portion of nanotubes are of the (m,n) type.

91. A macroscopic carbon fiber comprising at least about  $10^6$  single-wall carbon nanotubes in generally parallel orientation.

92. The fiber of claim 91 comprising at least about  $10^6$  single-wall carbon nanotubes.

93. A composite fiber comprising a plurality of the fibers of claim 91.

94. A molecular template array for growing continuous length carbon fiber comprising a segment of the fiber of claim 91.

95. The fiber of claim 91 having a length of at least 1 millimeter.

96. The fiber of claim 91 wherein a substantial portion of said  
5 nanotubes are of the (n,n) type.

97. The fiber of claim 91 wherein all of said nanotubes are not of the same type.

98. A composite article of manufacture comprising a matrix material selected from the group consisting of metals, polymers, ceramics and cermets, said  
10 matrix having embedded in at least a portion thereof a property enhancing amount of the carbon fibers of claim 91.

99. The composite article of claim 98 wherein said property is structural, mechanical electrical, chemical, optical, or biological.

100. A high voltage power transmission cable wherein at least one  
15 conductor comprises a continuous carbon fiber according to claim 96.

101. The power transmission cable of claim 100 wherein both a central conductor and a coaxially disposed outer conductor are formed from said carbon fiber and an insulating layer is disposed therebetween.

102. The power transmission cable of claim 101 wherein said insulating  
20 layer is an air space.

103. The power transmission cable of claim 101 wherein said insulating layer comprises a material selected from the group consisting of insulating carbon fiber made from carbon nanotubes of the (m,n) type and insulating BN fiber made from hexabornitride nanotubes or mixtures thereof.

104. A solar cell for converting broad spectrum light energy into  
25 electrical current comprising a molecular array according to claim 81 as the photon collector.

105. The solar cell of claim 104 additionally comprising a photoactive dye coupled to the upper ends of the nanotubes in said array.



106. A bistable, nonvolatile memory bit comprising the endohedrally-loaded tubular carbon molecule of claim 77.

107. The memory bit of claim 106 wherein the tubular carbon molecule is formed from a (10,10) type nanotube and the endohedral species is a  $C_{60}$  or  $C_{70}$  fullerene molecule.

108. A bistable, nonvolatile memory device comprising the memory bit of claim 106, means for writing to said bit and means for reading said bit.

109. The memory device of claim 108 wherein said means for writing comprises a nanocircuit element adapted to direct a voltage pulse of positive or negative polarity at said bit to cause said endohedral species to move from a first end to a second end of said bit.

110. The memory device of claim 108 wherein said means for reading said bit comprises

(a) a first nanocircuit element adapted to be biased at a first voltage ( $V_{read}$ ) and spaced from a read end of said bit to form a first gap therebetween; and

(b) a second nanocircuit element adapted to be biased to ground voltage ( $V_G$ ) and spaced from said read end of said bit to form a second gap, whereby the presence of said endohedral species is unambiguously determined by the presence of current tunnelling across said first and second gaps.

111. A microporous anode for an electrochemical cell comprising a molecular array according to claim 81.

112. A lithium ion secondary battery comprising the anode of claim 111, a cathode comprising  $LiCoO_2$  and an aprotic organic electrolyte wherein a fullerene intercalating compound (FIC) of lithium forms at the anode under charging conditions.

113. An apparatus for forming a continuous macroscopic carbon fiber from a macroscopic molecular template array comprising at least about  $10^4$  single-wall carbon nanotubes having a catalytic metal deposited on the open ends of said nanotubes, said apparatus comprising:

- (a) means for locally heating only said open ends of said nanotubes in said template array in a growth and annealing zone to a temperature in the range of about 500°C to about 1300°C;
- (b) means for supplying a carbon-containing feedstock gas to the growth and annealing zone immediately adjacent said heated open ends of said nanotubes in said template array; and
- (c) means for continuously removing growing carbon fiber from said growth and annealing zone while maintaining the growing open end of said fiber in said growth and annealing zone.
114. The apparatus of claim 113 wherein said means for locally heating comprises a laser.
115. The apparatus of claim 113 enclosed in a growth chamber maintained at a vacuum by evacuation means.
116. The apparatus of claim 115 further comprising a vacuum feed lock zone through which said continuously produced carbon fiber is passed and a take-up roll at atmospheric pressure.
117. A composite material comprising:
- (a) a matrix; and
- (b) a plurality of single-wall carbon nanotubes embedded within said matrix.
118. The composite material of claim 117, wherein said matrix comprises a polymer.
119. The composite material of claim 118, wherein said polymer comprises a thermosetting polymer.
120. The composite material of claim 119, wherein said thermosetting polymer is selected from the group consisting of phthalic/maleic type polyesters, vinyl esters, epoxies, phenolics, cyanates, bismaleimides, and nadic end-capped polyimides.
121. The composite material of claim 118, wherein said polymer comprises a thermoplastic polymer.

122. The composite material of claim 121, wherein said thermoplastic polymer is selected from the group consisting of polysulfones, polyamides, polycarbonates, polyphenylene oxides, polysulfides, polyether ether ketone, polyether sulfones, polyamide-imides, polyetherimides, polyimides, polyarylates, and liquid crystalline polyesters.

123. The composite material of claim 117, wherein said matrix comprises a metal.

124. The composite material of claim 117, wherein said matrix comprises a ceramic.

125. The composite material of claim 117, wherein said matrix comprises a cermet.

126. The composite material of claim 117, wherein said carbon nanotube material comprises tubular carbon nanotube molecules.

127. The composite material of claim 117, wherein said carbon nanotube material comprises ropes of up to about  $10^3$  SWNTs.

128. The composite material of claim 117, wherein said carbon nanotube material comprises fibers of greater than  $10^6$  SWNTs.

129. The composite material of claim 126, 127, or 128, further comprising an additional fibrous material.

130. The composite material of claim 126, 127, or 128, wherein said carbon nanotube material is modified to interact with said matrix material.

131. A method for producing a composite material containing carbon nanotube material comprising:

- (a) preparing a matrix material precursor;
- (b) combining single-wall carbon nanotubes with said matrix material precursor; and
- (c) forming said composite material.

132. The method of claim 131, wherein said carbon nanotube material is combined with said matrix material precursor before said step of forming.

133. The method of claim 131, wherein said carbon nanotube material is combined with said matrix material precursor during said step of forming.

134. The method of claim 131, wherein said carbon nanotube material is combined with said matrix material precursor immediately after said step of forming.

135. The method of claim 131, wherein said matrix material precursor is caused to flow around a pre-formed arrangement of said carbon nanotube material.

136. A method of producing a composite material containing carbon nanotube material comprising:

- (a) preparing an assembly of a fibrous material;
- (b) adding single-wall carbon nanotubes to said fibrous material; and
- (c) adding a matrix material precursor to said carbon nanotubes and said fibrous material.

137. The method of claim 136, wherein said fibrous materials are arranged in a two-dimensional sheet, and some portion of said carbon nanotubes are oriented in a direction other than parallel to said sheet.

138. The method of claim 131 or 136 wherein said carbon nanotubes comprise tubular carbon nanotube molecules.

139. The method of claim 131 or 136, wherein said carbon nanotubes comprise ropes of up to about  $10^3$  SWNTs.

140. The method of claim 131 or 136, wherein said carbon nanotubes comprise fibers of greater than  $10^6$  SWNTs.

141. A three-dimensional structure that self-assembles from derivatized single-wall carbon nanotube molecules comprising:

a plurality of multifunctional single-wall carbon nanotubes assembled into said three-dimensional structure.

142. The three-dimensional structure of claim 141, wherein said single-wall carbon nanotubes have multifunctional derivatives on their end caps.

143. The three-dimensional structure of claim 141, wherein said single-wall carbon nanotubes have multifunctional derivatives at multiple locations on said single-wall carbon nanotubes.

144. The three-dimensional structure of claim 141, wherein said single-wall carbon nanotubes are assembled as a result of van der Waals attractions.

145. A three-dimensional structure of claim 141, which has electromagnetic properties.

146. The three-dimensional structure of claim 145, wherein said electromagnetic properties are determined by a functionally-specific agent.

147. A three-dimensional structure of claim 141, which is symmetrical.

148. A three-dimensional structure of claim 141, which is not symmetrical.

149. A three-dimensional structure of claim 141, which has biological properties.

150. A three-dimensional structure of claim 149, which operates as a catalyst for biochemical reactions.

151. A three-dimensional structure of claim 149, which interacts with living tissue.

152. A three-dimensional structure of claim 149, which serves as an agent for interaction with functions of a biological system.

153. A light harvesting antenna comprising:  
at least one single-wall carbon nanotube conductive element, said at least one nanotube having a length selected relative to a desired current level and a desired voltage level.

154. The light harvesting antenna of claim 153, wherein said at least one single-wall carbon nanotube forms a Schottky barrier.

155. An array of light harvesting antennas of claim 153.

156. The array of light harvesting antennas of claim 155, wherein said array is formed by self-assembly.

157. A molecular electronic component comprising at least one single-wall carbon nanotube.

158. The molecular electronic component of claim 157, wherein said molecular electronic component is a bridge circuit for providing full wave rectification, said bridge circuit comprising:

four single-wall carbon nanotubes, each of said four single-wall carbon nanotubes forming one edge of a square and linked to two of four buckyballs, each of said four buckyballs located at a corner of said square.

159. The bridge circuit of claim 158, wherein said buckyballs and single-wall carbon nanotubes are derivitized to include functionally specific linking agents.

160. A molecular electronic component of claim 157, which is a fullerene diode.

161. A nanoscale manipulator comprising at least one single-wall carbon nanotube.

162. The nanoscale manipulator of claim 161, which is nanoforceps.